

The achievement of n-type doping by sulfur in diamond is controversial.^{1,2,3} In this work, diamond films were grown in a microwave reactor using H₂S as the sulfur source. The S/C atomic ratio was varied from 15 to 20,000 ppm; the methane concentration from 0.1 - 0.4%. In some experiments, co-doping of sulfur and boron was attempted by including trimethylboron (TMB) in the source gases. Single crystal diamond with {111}, {110}, {100} faceting and n-type silicon wafers were used as substrates. The gas flow was 200 sccm, the pressure was 25 torr, and the microwave power was 1020 W. Substrate temperatures ranged from 700 to 750°C.

The samples were analyzed for sulfur by Secondary Ion Mass Spectroscopy (SIMS) and Particle-Induced X-ray Emission (PIXE). These results indicated no detectable sulfur-incorporation when H₂S was the lone dopant source. When TMB was also used, the observed sulfur concentration was just at the level of detection for PIXE. Additional tests are required to better clarify the sulfur concentration. Other experiments were performed in which diamond substrates were treated in an H₂/H₂S (H₂S concentration was 0.001%) plasma at 25 torr for 12 hours without CH₄ in the gas. These samples exhibited some of the same electrical and electrochemical properties as samples in which diamond growth occurred in the presence of H₂S.

Resistivity and electrochemical measurements do indicate that sulfur is affecting the electrical properties of diamond. However, this effect may be caused by surface effects rather than bulk changes. The impedance spectra showed a differential-capacitance frequency dependence represented by a constant phase element (CPE) in the equivalent circuit. A Mott-Schottky plot taken from a diamond grown with a gas-phase S/C atomic ratio of 6x10⁻⁵ is shown in Figure 1. The slope of the line is positive indicating n-type carriers. The uncompensated donor concentration was calculated from the slope and found to be 1.7x10¹⁷cm⁻³. From the intercept the flat-band potential is ~ 0.4 V vs. Ag/AgCl. Also, under ultraviolet illumination at 254 nm the open-circuit photopotential shifts to negative values, as expected for an n-type semiconductor. Similar results to those shown in Figure 1 were obtained by simply treating a virgin macle under a H₂/H₂S plasma.

The Mott-Schottky plot from a typical heavily boron-doped diamond is shown in Figure 2a. The slope indicates p-type conduction with an acceptor concentration of 2.3x10¹⁹ cm⁻³. The intercept shows a flatband potential of ~ 1.3 V vs. Ag/AgCl, in substantial agreement with other measurements.⁴ The open circuit potential of this sample shifted to positive values under ultraviolet illumination. This macle was then treated under the H₂/H₂S plasma for 12 hours. The results are shown in Figure 2b. The maximum at 0.6 V Ag/AgCl has been seen in several other samples and is suggestive of rapid surface states located in the forbidden gap.⁵ The data were analyzed using the methods of reference 5 and indicate the possible presence of surface states localized at 0.7 eV above the Fermi level.

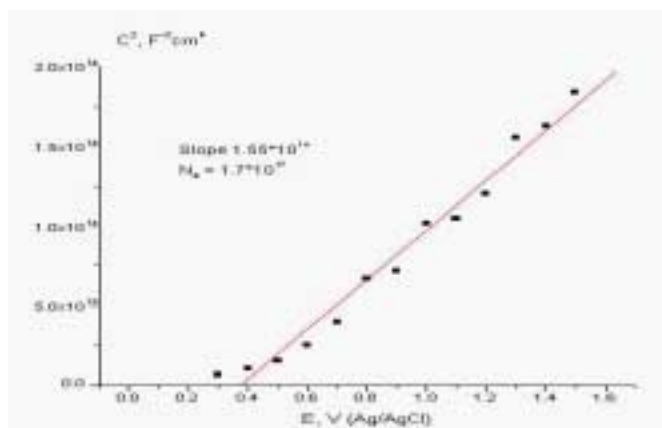
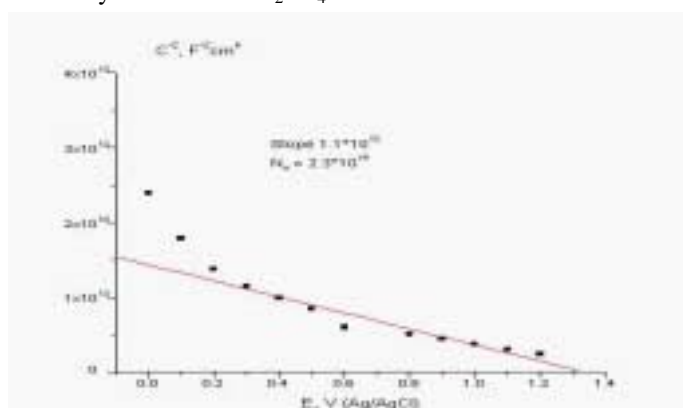
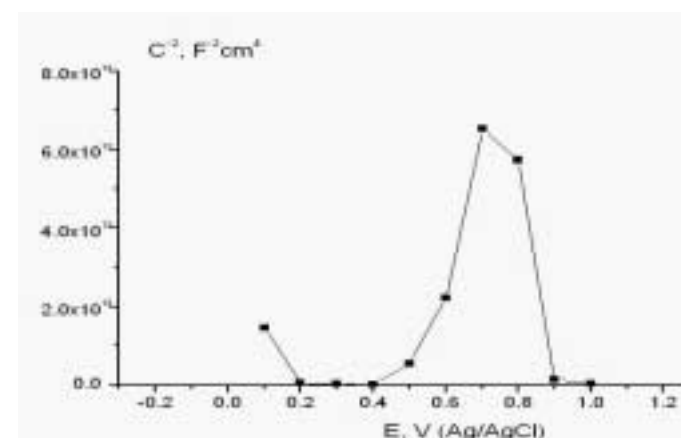


Figure 1. Mott-Schottky plot from (111) surface of diamond grown with a S/C ratio in the gas phase of 60 ppm. The positive slope indicates n-type conductivity. The number of donors, N_D , is $1.7 \times 10^{17} \text{ cm}^{-3}$. The electrolyte was 0.5 M H₂SO₄.



(a)



(b)

Figure 2. (a) Mott-Schottky plot obtained from (111) surface of a heavily B-doped macle. The number of acceptors, N_A , is $2.3 \times 10^{19} \text{ cm}^{-3}$. (b) Mott-Schottky plot of the same macle after plasma treatment in a H₂/H₂S environment. The electrolyte was 0.5 M H₂SO₄.

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